

FRACTAL ANALYSIS OF GRANULAR ACTIVATED CARBONS USING ISOTHERM DATA

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INTRODUCTION

Utilization of adsorption on solid surfaces was exercised for the first time in 1785. Practical application of unactivated carbon filters, and powdered carbon were first demonstrated in the American water treatment plant, and a municipal treatment plant in New Jersey, in 1883 and 1930, respectively. The use of activated carbon became widespread in the next few decades. At present, adsorption on carbons has a wide spread application in water treatment and removal of taste, odor, removal of synthetic organic chemicals, color-forming organics, and disinfection by-products and their naturally occurring precursors.

Along with the application of adsorption, the theoretical study has been more and more profound. The concept of adsorption isotherm introduced to specify the equilibrium surface concentration of adsorbate on adsorbent as a function of bulk concentration of adsorbate. The three famous mathematical models Langmuir, BET, and Freundlich were developed to describe the adsorption isotherm for single adsorbates. Langmuir adsorption isotherm describes equilibrium between surface and solution as a reversible chemical equilibrium between species. Adsorbent surface is considered to be made up of fixed individual sites where molecule of adsorbate, may be chemically bounded. Each site is assumed to be capable of binding at most one molecule of adsorbate. Langmuir model allows accumulation only up to a monolayer while the total amount of mass adsorbed is assumed to approach a saturating value when concentration becomes very large. Since both BET and Freundlich models were used in this study, settings of these models are presented.

The BET adsorption isotherm, extended the Langmuir model from a monolayer to several molecular layers. Model assumes that above the monolayer, each additional layer of adsorbate molecules is in equilibrium with the layer below it. Therefore layers of different thickness are allowed to co-exist. Under this circumstances, the process of sorbing a new layer of adsorbate onto old layers is assumed to be identical to the process of condensing adsorbate from solution to solid or liquid. The resulting isotherm is known to have the form of:

$$\frac{V}{V_m} = \frac{cX}{1-X} \sum_{n=1}^{\infty} B_n \left(\frac{1-(n+1)X^n + nX^{n+1}}{1+(c-1)X - cX^{n+1}} \right) \quad (1)$$

In this model, V is the volume of adsorbate per mass of adsorbent at equilibrium, V_m is the volume of monolayer adsorbate per mass of adsorbent, c is a dimensionless constant that is related to the difference in free energy between adsorbate on the first and successive layers, n represents the number of layers adsorbed, B_n is the fraction of adsorbent surface that is covered by n layers of adsorbate, and X is the value of p/p_0 (p = equilibrium partial pressure of adsorbate, p_0 = the saturated vapor pressure). The parameter B_n introduces the unsimilarity between the area at the n th layer and adsorbent surface, for adsorbents with uneven surfaces. Traditionally, since B_n is difficult to be determined, it is assumed that all layers have the same surface area as that of the adsorbent, and therefore an infinite number of layers of adsorbate would be expected. The summation in the above equation has a single term with $B_n = 1$ for $n = \infty$. Recently using fractal theories parameter B_n has been estimated for fractal surfaces.

For low concentration systems ($X \ll 1$) the BET model can be simplified as:

$$\frac{X}{V(1-X)} = \frac{1}{V_m c} + \frac{c-1}{V_m c} X \quad (2)$$

The BET adsorption isotherm suggests that surface concentration reaches a plateau as the monolayer is filled, then increases proportional to increase in p . Langmuir and BET models incorporate an assumption that the energy of adsorption is the same for all surface sites and not dependent on degree of coverage. In reality, the energy of adsorption may vary because real surfaces are heterogeneous.

Another isotherm model which has been used widely is the Freundlich adsorption isotherm. This model attempt to account for energy of adsorption, assuming that, the frequency of sites associated with a free energy of adsorption decreases exponentially with increasing free energy. The Freundlich isotherm has the form of $q = k C^{1/n}$, where k and n are constants. In this model the surface concentration of adsorbate does not approach a saturating value as C increases, since there are always surface sites with higher free energies of adsorption to fill. The Freundlich

isotherm is very widely used to fit observed data empirically even when there is no basis for its underlying assumptions.

Fractal Dimension

Fractal geometry is a mathematical tool for dealing with complex systems that have no characteristic length scale. The scale-invariant systems, are usually characterized by noninteger or "fractal" dimensions. The concept of fractal dimension, d , can be expressed as how the mass $M(L)$ changes with the linear size L of the system with uniform density. In fractal systems, a smaller part of the system of linear size bL ($b < 1$), the $M(bL)$ is decreased by a factor of b^d , such as $M(bL) = b^d M(L)$. Simply we can assume that $M(L) = AL^d$, with A being constant.

The Koch Curve is one of the most common deterministic fractals. In Koch curve, by each iteration the length of the curve is increased by a factor of 4/3. The mathematical fractal then is defined in the limit of infinite iterations, $n \rightarrow \infty$, where the total length of the curve approaches infinity. If the linear size is decreased by a factor of $b = 1/3$, the total length (mass) of the curve will be decreased by a factor of $1/4$ (i.e., $M(\frac{1}{3}L) = \frac{1}{4}M(L)$). Therefore, it can be assumed that $1/4 = (1/3)^d$, and $d = \log 4 / \log 3$. Such non integer dimensions are called "fractal dimension" and those objects described by a fractal dimension are called fractals.

Applying fractal dimension theory, one can derive different methods to measure the dimension of a fractal surface. In the traditional adsorption theories, the adsorbent's surface is simplified to be a locally flat surface, giving $d = 2$. But many adsorbents' surfaces are sufficiently porous and irregular. For example, the radius of micropores in activated carbon can be smaller than 1 nm, while that of the macropores can be bigger than 25 nm. For such surfaces, a minor changes in the size of adsorbate molecules can result in a great change for monolayer coverage.

The geometrical complexity of the surface of many irregular adsorbents, such as activated carbons and wood suggests that, surfaces structure of these adsorbents can be easily described according to the fractal theory. The fractal dimension " d " then would be a measure of adsorbent's surface irregularity. Recent studies showed that, values of " d " that expresses the degree of complexity of surface and/or porous structure, fall in the range of 2-3, representing extremely heterogeneous surfaces (Pfeifer et al., 1983, Jaroniec and Kruk, 1997). A specific value of " d " demonstrate self similarity, showing that any section of surface unfolds into m^d similar sections upon m -fold magnification. A dimension higher than 2 implies that any monolayer on a surface with $d > 2$ correspond to a three dimensional bulk rather than a two dimensional film. Under this condition, the number of adsorption sites within distance L from any fixed site grows as L^d .

Many methods have been developed in order to obtain " d " on the basis of adsorption, mercury porosimetry, scanning electron microscopy, and small-angle X-ray and neutron scattering measurements (Jaroniec and Kruk, 1997). Among those, adsorption method play an important role. Some of the fractal oriented adsorption theories are simple and convenient since they require only one complete adsorption isotherm for a given solid to calculate the value of " d ".

This paper presents the results of a study conducted to investigate the extent of association between surface fractal dimension and adsorption capacity of a group commercial and disorder carbons, using BET isotherm data and a model proposed by Segars et al., 1996.

STUDY APPROACH

The purpose of this study was to: a) use an appropriate model and gas phase isotherm adsorption data to estimate fractal dimensions of a range of carbons with different surface structure, and b) propose a model that can predict adsorption capacity of carbons in a single component liquid phase system, using estimated fractal dimensions.

Study was conducted in four steps: 1) using volumetric isotherm test (BET test), adsorption-desorption isotherms of nitrogen on selected carbons were determined, 2) using a model proposed by Segars et al., 1996, and gas phase isotherm data, fractal dimensions and other specific surface parameters were evaluated, 3) liquid phase isotherm data were determined using a single component liquid phase system containing phenanthrene-9- ^{14}C , and 4) a modified adsorption model that relates liquid phase adsorption capacity to the surface dimension " d " was proposed. While liquid phase modeling is in progress, the obtained results of fractal analysis are presented.

RESULTS

Volumetric (gas phase) isotherm data were determined for two granular activated carbons (GAC 1240 and Sorbonorite 4), and four disorder carbons synthesized at the Argonne National Laboratory, using clay as templates (carbons # 1 to 4). An example of the adsorption-desorption isotherms for these carbons are presented in Figures 1. As it is shown adsorption type II and III were observed for these carbons. Using volumetric isotherm data and modified BET model proposed by Segars et al., 1996 (this model introduces the fractal dimension to the adsorption isotherms), important parameter B_n in BET model was estimated as follows:

$$B_n = \left(\frac{r}{L}\right)^{d-d_{n-1}} - \left(\frac{r}{L}\right)^{d-d_n}, \text{ where :}$$

$$d_{n+1} = [1 - LN(\frac{r}{L})] - \sqrt{[1 - LN(\frac{r}{L})]^2 + 2[d_n * LN(\frac{r}{L}) + (d-2) * LN2 - LN(3-d_n)]}$$

The fitting parameters to the model were the gas phase isotherm adsorption data. The pressure p was ranging from 0 to p_0 and parameter "r" was the size of adsorbed molecule. The computer simulation predicted parameters : d , r/L , V_m , c , and the maximum number of adsorbed layer, N . The results of modeling simulation are provided in Table 1. As it is indicated fractal dimension of commercial carbons were above 2.5, endorsing a non- flat surface structure for these adsorbents. However the modeled "d" for disorder carbons were about 2.1 representing relatively flat surfaces. For comparison, the V_m values estimated by the traditional BET model are also included in the Table 1. The estimated standard deviation for V_m indicated that model can accurately predict the volumetric isotherm data, using estimated parameters. Figures 2, shows examples of the modeled (line) and measured isotherm curves for these carbons. In general results of modeling showed that modified BET model can accurately estimate gas phase adsorption isotherms, and adsorption for these carbons matches type II adsorption isotherm better than type III.

The liquid phase adsorption isotherms were evaluated for carbons from measured concentration of Phenanthrene-9-¹⁴C at equilibrium, using Freundlich isotherm model ($q = kC^{1/n}$). Table 2 shows calculated adsorption capacity k , and degree of bonding , $1/n$ for all six carbons. The adsorption capacity of disorder carbons was much lower than commercial carbons. The liquid phase adsorption data were in a good agreement with the results of fractal modeling, suggesting that carbons with fractal surface have higher adsorption capacity in liquid phase systems.

CONCLUSION

Using a modified BET isotherm model and volumetric isotherm data, fractal dimensions of two commercial carbons, GAC 1240 and Sorbonorite 4, were estimated. The fractal dimension "d" for these carbons were about 2.7 and 2.6 respectively. The estimated monolayer volumes for these two carbons were 25-27 % larger than the volumes determined by BET. The disordered (synthesized) carbons showed a surface dimension of near 2, representing a flat surface. The monolayer volumes for these four disordered carbons were similar to the results of BET analyses. Liquid phase isotherm data showed a much higher adsorption capacity for commercial carbons with fractal dimension than disorder carbons. Development of a model that can predict liquid phase adsorption capacity of these adsorbents as a function of their surface dimensions is in progress.

ACKNOWLEDGMENT

Part of this work was performed under the auspices of the Office of Basic Energy Sciences, Division of Chemical Sciences, U.S. Department of Energy, under contract number W-31-109-ENG-38.

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Table 1. Estimated Surface Parameters Using Modified BET Model

Adsorbent		d	r/L	C	N	V _m	S
Sorbonorite 4	fractal	2.7	0.1	100	11	405	4.24
	B.E.T.	--	--	99	--	293	
GAC 1240	fractal	2.6	0.1	250	45	282	2.03
	B.E.T.	--	--	67	--	210	
Carbon #1	fractal	2.1	1E-5	90	90	48	21.1
	B.E.T.	--	--	107	--	55.5	
Carbon #2	fractal	2.2	1E-5	31.2	45	1.39	0.25
	B.E.T.	--	--	23.8	--	1.36	
Carbon #3	fractal	2.45	0.01	400	95	115	10.6
		--	--	111	--	100	
Carbon #4	fractal	2.1	1E-6	90	90	6.57	3.08
	B.E.T.	--	--	406	--	6.68	

D=fractal dimension

C= constant

r/L= ratio of molecule radius to the linear size of fractal system

N= number of layers

V_m= volume of a monolayer

$$s = \sqrt{\frac{\sum_{i=1}^n (y_i - \bar{y})^2}{n-2}} = \text{standard deviation of the volume adsorbed. } n \text{ is the number of data point,}$$

\bar{y}_i is the modeled volume.

Table 2. Calculated Freundlich Adsorption Isotherm Parameters

	Sorbonorite 4	GAC 1240	Carbon #1	Carbon #3	Carbon #4
k	332	278	0.09	0.08	3.19
1/n	0.77	0.79	0.37	0.35	0.59
R ²	0.92	0.96	0.92	0.89	0.96

* Carbon #2 presented inconclusive results

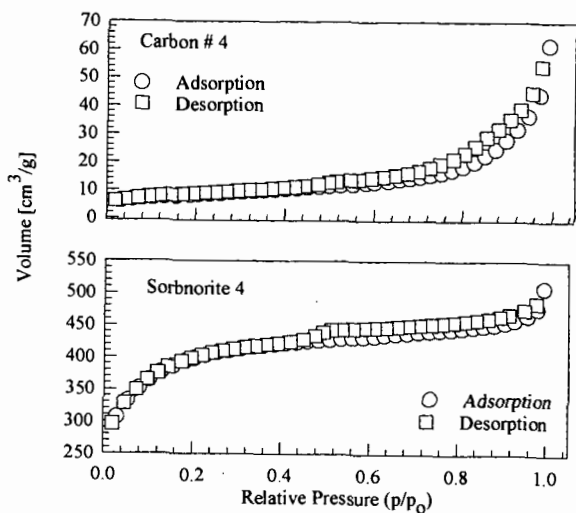


Figure 1. Adsorption and Desorption Isotherms Determined for Carbon #4 and Sorbonorit 4

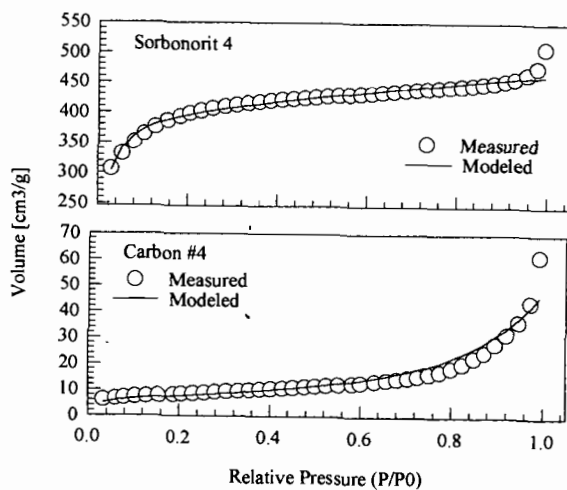


Figure 2. Modeled and Measured Adsorption Isotherms For Sorbonorit 4 and Carbon #4.